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Excessive Thermodynamic Properties of Praseodymium in a Gallium–Indium Alloy

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Abstract—The equilibrium potentials of praseodymium-diluted homogeneous Pr–Ga–In alloys in a (Li–K–Cs)Cl_{eut}-based salt electrolyte were measured between 573–1073 K by the emf method. These potentials are used to calculate the activity coefficients of α-praseodymium in liquid Ga–In eutectic alloys. $PrIn_3$ alloy with well-known thermodynamic characteristics and without phase transitions in the temperature range 428–1483 K was employed as the reference electrode.

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INTRODUCTION

Non-aqueous regeneration methods, among them electrochemical ones, are developed using heat- and radiation-resistant salt and metallic melts for rapid reprocessing of highly irradiated short-stored nuclear fuel (INF) from fast neutron reactors. A necessary prerequisite for developing such technologies is the existence of reliable thermodynamic information on the state of elements to be separated in salt and metallic melts.

Promising metallic systems for developing the technology of regeneration of irradiated fuel are low-melting-point compositions based on Group III elements such as Al, Ga, and In. Rare-earth metals are present among the nuclear fuel fission products in large amounts; for example, 1 t INF contains up to 2.8 kg praseodymium. Therefore, the aim of this work was to study the thermodynamic properties of alloys of praseodymium with the eutectic Ga–In alloy, which melts at 15.7–15.9°C.

EXPERIMENTAL

In this study, the electrode potentials of the alloys were measured versus reference electrode by compensation method employing an Autolab PGStat 302 N potentiostat–galvanostat at zero current. The emf of the galvanic cell

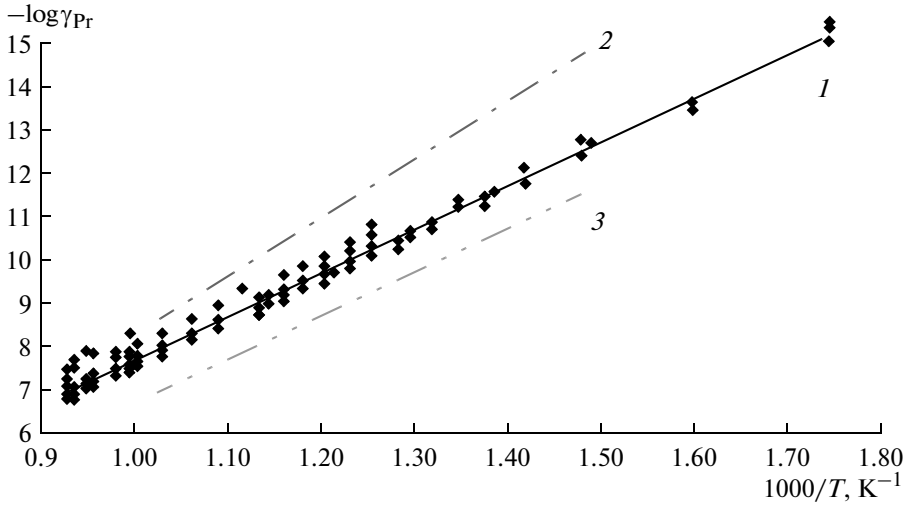
$$(-)\ \text{Liquid} + PrIn_3\ |LiCl–KCl–CsCl + PrCl_3|\ Pr–Ga–In\ (+) \quad (1)$$

was measured in a cell similar to that described in [1] and manufactured of stainless steel and equipped with a side-arm. The cell was connected via the side-arm to a vacuum line, a system of inert gas (Ar) purification, and an expandable gas receiver, which allowed to maintain Ar pressure inside the cell at atmospheric pressure during the entire experiment.

In our experiments, we used metals and salts of the following purity (wt %): metallic single-crystal gallium (≥99.9999%) according to TU 48-4-350–84, metallic indium IN-000 (≥99.999%) according to State Standard GOST 10297–75, praseodymium oxide PrO-L (≥99.99%) according to TU 48-4-523–90, metallic praseodymium PrM-1 (≥99.8%) according to TU 48-1-215–72, ROTH lithium chloride (≥99%), OSCh 17-2 cesium chloride, and OSCh 5-4 potassium chloride.

The individual salts and the eutectic mixture of lithium, potassium, and cesium chlorides were prepared by the technique described in [2, 3]. LiCl–KCl–CsCl eutectic mixture containing praseodymium trichloride was prepared by reacting praseodymium oxide in a salt melt with gaseous hydrogen chloride. The praseodymium concentration in the salt melt was determinated by chemical analysis [4]. The final salt melt ($C_{Pr} \approx 2$ wt %) was stored in an inert atmosphere.

Eutectic Ga–In alloys containing 21.8 wt % indium were prepared by fusing individual metal samples at a temperature of 50°C. In our experiments, a liquid alloy was placed into small beryllium oxide crucibles of beryllium oxide 2 cm^3 in volume with a dozing pipette; then its mass was measured and a required amount of metallic praseodymium added. The small crucibles (up to 20 at a time) were placed into a large beryllium oxide crucible with a volume of 300 cm^3, metallic conductors made of 0.2 mm diameter tungsten wire inserted into alumina capillaries were introduced into the small crucibles, and the small crucibles



Activity coefficients of α-Pr in alloys: (*1*) In–Ga (this work), (*2*) Ga [9], and (*3*) In [8].

were covered with the eutectic LiCl–KCl–CsCl mixture containing praseodymium trichloride. Alloys containing less than 0.8 wt % Pr were prepared directly in experiments by the cathodic deposition of praseodymium on a Ga–In alloy using praseodymium-rich Pr–In alloys as an anode (reference electrode in galvanic cell (1)).

Preparation of the initial Ga–In melt, loading of the alloy components and electrolyte into prepared experimental cells were performed in an inert atmosphere (Ar) in a MBraun Unilab 1200/780 glove box. The cell was hermetically sealed, placed in a resistance furnace with automatic temperature control, heated to 923–973 K, and held at this temperature for 12 h for homogenization. The electrode potentials of the alloys were measured relative to an L + $PrIn_3$ alloy. The praseodymium concentration in the alloy corresponded to the two-phase state [5] (i.e., saturated solution of praseodymium in liquid indium in equilibrium with intermetallic compound $PrIn_3$) and varied from 8.7 to 12.1 mol % Pr.

At a constant temperature, the alloy potentials were considered to be equilibrium if they had no tendency to a monotonic shift and changed by no more than 0.1–0.5 mV within 1 hour. In this case, the potentials of alloys of the same phase composition were reproducible within ±(0.1–0.2) mV. During one experiment, the temperature range 573–1073 K was passed several times from top to bottom and from bottom to top with a step of 30–50°C. The temperature was controlled by a thermocouple (type K) inserted in a beryllium-oxide sheath and placed directly into a melt.

On completion of the experiment, the cell was cooled, the alloys were washed out with ice (273–278 K) deionized water and analyzed to determine the praseodymium content on an ELAN 9000 mass spectrometer at the certified Analytical Test Center—Russian Arbitration Laboratory for Testing Nuclear Power Engineering Materials.

RESULTS AND DISCUSSION

To relate the potentials of the two-phase liquid-metal reference electrode (L + $PrIn_3$) to the potential of metallic praseodymium, in an additional series of experiments the emf of galvanic cell (2)

$$(-)\ \mathrm{Pr}\ |\mathrm{LiCl–KCl–CsCl} + PrCl_3|\ \mathrm{L} + PrIn_3\ (+), \quad (2)$$

was measured.

Since praseodymium undergoes the α-Pr → β-Pr phase transition at 1069 K, the corresponding corrections were introduced into the values of emf measured at temperatures above this point [6].

The experimental dependence $E = f(T)$ of cell (2) is adequately approximated between 573–1073 K by the straight-line equation

$$E = (0.7914 - 0.2927 \times 10^{-3} T) \pm 2.0687\sqrt{3.15 \times 10^{-5}\left(\frac{1}{25} + \frac{(T - 760.08)^2}{587420}\right)},\ \mathrm{V}, \quad (3)$$

which is presented according to the recommendations from [7].

In the range 573–1073 K, the activity of α-praseodymium in indium melts calculated by Eq. (3) is described by Eq. (4) and agrees well with the data from [8] obtained for a narrower temperature range,

$$\log a_{\alpha\text{-Pr(In)}} = (4.425 - 11965/T) \pm 2.0687\sqrt{0.013\left(\frac{1}{25} + \frac{(1/T - 0.00137)^2}{1.6 \times 10^{-6}}\right)}. \quad (4)$$

Excessive thermodynamic properties of α-Pr in alloys with Ga, In, and Ga–In eutectic

Metals	$-\Delta\overline{H_{Pr}}$, kJ/mol	$-\Delta\overline{S_{Pr}^{exc}}$, J/(mol K)	$-\Delta\overline{G_{Pr}^{exc}}$, kJ/mol			Source
			675 K	775 K	975 K	
Ga	259.8	102.1	190.9	180.7	160.3	[9]
In	191.7	64.1	148.4	142.0	129.2	[8]
Ga–In	191.4 ± 3.8	45.0 ± 4.2	161.0 ± 1.5	156.5 ± 0.9	147.5 ± 0.6	This work

The emf of galvanic cell (1) was calculated versus metallic praseodymium with allowance for the corrections for the α-Pr → β-Pr phase transition at 1069 K and using the emf sum rule.

The activity coefficients of α-praseodymium were measured using ternary Pr–Ga–In alloys not saturated by praseodymium as working electrodes. The activity coefficients of α-praseodymium were calculated from the emf of galvanic cell (1) and the praseodymium concentrations found from the chemical analysis.

In the studied temperature range, the dependence $\log\gamma_{\alpha\text{-Pr}} = f(T)$ in the eutectic Ga–In melt is approximated by Eq. (5),

$$\log\gamma_{\alpha\text{-Pr(Ga–In)}} = (2.351 - 9996/T) \pm 1.9726\sqrt{0.0394\left(\frac{1}{191} + \frac{(1000/T - 1.1087)^2}{3.948}\right)}. \quad (5)$$

The figure depicts the experimental data on the activity coefficients of α-praseodymium in Ga–In eutectic alloys in comparison with the available data on the activity coefficients of α-praseodymium in liquid gallium and indium based alloys.

The excessive thermodynamic properties of praseodymium in a liquid gallium-indium alloy were calculated from Eq. (5), and the results are listed in the table.

The praseodymium activity coefficients in homogeneous Pr–Ga–In alloys occupy intermediate values between those in alloys with individual gallium (Pr–Ga) and indium (Pr–In). As the temperature decreases, the values of $\log\gamma_{Pr}$ in the Ga–In eutectic alloy are gradually shifted from the binary Pr–Ga system to the Pr–In system.

CONCLUSIONS

The emf of galvanic cells measured between 573–1073 K were used to determine the activity coefficients of α-praseodymium and its excess thermodynamic characteristics in the Ga–In eutectic alloy. As the temperature increases, the effect of gallium on the activity coefficients of praseodymium in ternary alloys increases, which is likely due to an increase in the interparticle interaction of praseodymium with gallium in homogeneous liquid Pr–Ga–In alloys.

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